

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
4 October 2001 (04.10.2001)

PCT

(10) International Publication Number  
**WO 01/72863 A1**

- (51) International Patent Classification<sup>7</sup>: C08G 18/00, C08J 9/00, 9/14
- (21) International Application Number: PCT/US01/09626
- (22) International Filing Date: 26 March 2001 (26.03.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
60/192,231 27 March 2000 (27.03.2000) US
- (71) Applicant (for all designated States except US): APACHE PRODUCTS COMPANY [US/US]; 107 Service Road, P.O. Box 5287, Anderson, SC 29623-5287 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): BURGESS, James, H. [US/US]; 105 West Round Hill Road, Greenville, SC 29609 (US). GLORIOSO, Sammie, J. [US/US]; 107 Claimont Drive, Ridgeland, MS 39157 (US).
- (74) Agents: VOLPE, Anthony, S. et al.; Volpe and Koenig, P.C., Suite 400, One Penn Center, 1617 John F. Kennedy Boulevard, Philadelphia, PA 19103 (US).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MY, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:  
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/72863 A1

(54) Title: FIRE RESISTANT FOAM AND FOAM PRODUCTS, METHOD AND DISPERSIONS FOR MAKING SAME

(57) Abstract: A synthetic polymer foam is produced which incorporates fine particles of expandable graphite which surprisingly impart excellent fire resistant properties to the foam, particularly to foam made with a non-halogenated hydrocarbon as the primary blowing agent. For best results, the foam is produced through mixing the constituent materials, including the expandable graphite using a screw extruder. The foam can also be produced by creating a graphite/polyol or graphite/isocyanate dispersion in an extruder then mixing the remaining components in a conventional batch mixing or high pressure spraying process. Alternatively, conventional mixing can be used for the entire process, but use of a screw extruder in whole or in part is preferred.

[0001]        **FIRE RESISTANT FOAM AND FOAM PRODUCTS,  
METHOD AND DISPERSIONS FOR MAKING SAME**

[0002]        This application claims priority from U.S. Provisional Application No. 60/192,231, filed March 27, 2000.

[0003]        The present invention relates to foam and foam products having excellent fire resistance achieved through the use of expandable graphite. In particular, the foam is preferably made using small particles of expandable graphite and a non-halogenated hydrocarbon as a primary blowing agent in an extrusion process. In preferred embodiments, rigid polyisocyanurate foam is made with expandable graphite particles having an average particle size less than 200 microns which exhibits self extinguishing properties and good insulation qualities.

[0004]                                **BACKGROUND**

[0005]        Foams and processes for their production are well known in the art. Such foams are typically produced by reacting ingredients such as a polyisocyanate with an isocyanate reactive material such as a polyol in the presence of a blowing agent.

[0006]        Synthetic foams have many uses and are produced in many forms. Rigid foam insulation panels are used in the construction of buildings. Foam bun stock is used for freezer insulation. Flexible foam is used in the manufacture of automobiles and furniture. Shaped foam products are used for building facades and ornamental effects for both interior and exterior uses.

[0007]        Foam products are generally highly flammable when made solely out of their basic components. A variety of materials have been used in the past for imparting fire resistance to foams. For example, standard liquid flame retardants such as TRIS (-

chloro-2-propyl) phosphate products, commercially available as ANTI-BLAZE 80 from Albright and Wilson and as PCF from Akzo Nobel have been conventionally used to increase the fire resistance of the foam. Such additives can be used to produce Factory Mutual Class 1 rated foam when organic halogenated hydrocarbons, such as 1,1-dichloro-1-fluorethane (HCFC-141b) are used as the primary blowing agent. However, similar foams made with non-halogenated hydrocarbons, such as iso-pentane and/or cyclopentane, used as the primary blowing agent fail to produce Factory Mutual Class 1 rated foam.

[0008] The use of expandable graphite as a fire retardant for polymer foams is generally known through the teaching of U.S. Patent No. 3,574,644. It has been shown that particle size has an impact on the effectiveness of expandable graphite as a fire retardant. For example, U.S. Patent 5,169,876 teaches the effective use of expandable graphite in a flexible polyurethane foam with a particle size of 300 to 1000 microns, but that use of expandable graphite having a particle size of less than 200 microns is ineffective.

[0009] It is desirable to produce foam and foam products having improved fire resistance and/or self extinguishing characteristics. Since the use of certain halogenated hydrocarbons may have detrimental environmental effects, it is also desirable to provide foam made with a non-halogenated hydrocarbon as the primary blowing agent.

#### [0010] SUMMARY

[0011] A synthetic polymer foam is produced which incorporates fine particles of expandable graphite which surprisingly impart excellent fire resistant properties to the foam, particularly to foam made with a non-halogenated hydrocarbon as the primary blowing agent. For best results, the foam is produced through mixing the constituent materials, including the expandable graphite using a screw extruder. The foam can also be produced by creating a graphite/polyol or graphite/isocyanate dispersion in an extruder

then mixing the remaining components in a conventional batch mixing or high pressure spraying process. Alternatively, conventional mixing can be used for the entire process, but use of a screw extruder in whole or in part is preferred.

[0012] Expandable graphite material having an average particle size of less than 200 microns, such as expandable graphite commercially available as GRAFGuard 160-80 (80 mesh, 177 microns) from UCAR Graph-Tech Inc., wherein sulfuric acid and nitric acid are encapsulated within the graphite can be used. A neutral grade of expandable graphite having a PH of at least 5, preferably 7, with an expansion threshold of 160°C, such as GRAFGuard 160-80 N, is preferred. Expandable graphite with very fine average particle size of 100 microns or less, such as GRAFGuard 160-150 N (150 mesh), can be used with a non-halogenated hydrocarbon blowing agent when employing an extruder to make rigid PUR/PIR foam. Preferably the foam formulation includes at least 1% loading of expandable graphite to produce a fire resistant foam and at least 3% loading to produce self extinguishing foam and foam products. When subjected to burning, the expandable graphite particles within the foam expand up to one hundred times the original diameter creating a graphite char that retains an excellent heat resistance in addition to providing self extinguishing properties.

[0013] Applicants have discovered that use of a unique combination of expandable graphite and carbon black produces an excellent foam product having both fire resistance and good insulating qualities, even where non-halogenated hydrocarbon blowing agents are employed in the manufacture of the foam.

[0014] It is an object of the present invention to provide foam and foam products having improved fire resistance.

[0015] It is a further object to provide various methods for making such foams including the use of an extruder and the use of non-halogenated hydrocarbon blowing agents.

[0016] It is a further object to employ small particle size expandable graphite and/or carbon black in the manufacture of such foam.

[0017] Other objects and advantages of the present invention will become apparent through a description of the presently preferred embodiments.

[0018] **BRIEF DESCRIPTION OF THE DRAWING(S)**

[0019] Figure 1 is a schematic illustration of an apparatus for extruding polymer foam, or dispersions for use in making such foam, in accordance with the teachings of the present invention.

[0020] Figure 2 is a cross-sectional side view of the extruder head of the extruder of Figure 1.

[0021] Figure 3 is a table reflecting a control example made without expandable graphite and with a non-halogenated hydrocarbon blowing agent.

[0022] Figure 4 is a table of three foam examples made in accordance with the teachings of the present invention.

[0023] Figure 5 is a table reflecting foam characteristics of the examples set forth in Figures 3 and 4.

[0024] Figure 6 is a table reflecting additional examples of extruder made isocyanurate foam reflecting control Example 5 and Examples 6 and 7 made in accordance with the teachings of the present invention.

[0025] Figure 7 is a table reflecting foam characteristics of the examples set forth in Figure 6 in comparison with additional prior art examples.

[0026] Figure 8 is a table of preferred boardstock formulations.

[0027] Figure 9 is a table of preferred bunstock formulations.

[0028] Figure 10 is a table of preferred dispersion formulations.

**[0029] DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)**

[0030] Foams in accordance with the present invention are preferably manufactured using an extruder, such as the extruder system 102 schematically illustrated in Figure 1. The extruder can be used for the entire process or to make a dispersion of expandable graphite and/or carbon black which is then used to make foam using any mixing method. Use of the extruder provides the best results, but other conventional mixing methods may be used.

[0031] The extrusion system 102 includes a single or twin screw extruder 104 and an associated reservoir system 106. The extruder 104 includes a series of barrels C1-C12 and an extruder head 120. Preferably a twin screw extruder is employed such as described in U.S. Patent 5,723,506 assigned to the assignee of the present invention.

[0032] The reservoir system 106 includes a plurality of reservoirs 150-156 from which the foam components are supplied. The reservoirs 150-156 feed the foam component materials to the barrels C1-C12 and head 120 of the extruder 104 via a network of feed lines and valves as illustrated.

[0033] In manufacturing foam using the extrusion system of Figure 1, expandable graphite particles are preferably provided to the extruder 104 at barrel C1 from a fill station 150. Additional expandable graphite and/or carbon black is preferably provided to the extruder 104 at barrel C4 from a fill station 152. Isocyanate solution is preferably mixed and fed to barrels C2 and C6 of the extruder 104 from reservoirs 151 and 153. The isocyanate solution may be optionally pre-mixed with a dispersing agent and/or surfactant at reservoirs 151 and 153 and provided to the extruder 104 with the isocyanate at barrels C2 and C6.

[0034] Polyol is preferably provided from a reservoir 155 and fed to the extruder 104 at barrel C9. Surfactant, curing agent and foaming agent is preferably pre-mixed with the polyol contained in the reservoir 155 and fed to the extruder 104 at barrel C9.

[0035] Foaming and/or blowing agents are preferably provided from a reservoir 154 and fed to the extruder 104 at barrel C8 without previous mixing with other components. Additionally, foaming and/or blowing agents may be mixed with the polyol at reservoir 155 prior to entry to the extruder 104 at barrel C9. For example, foaming agent is provided to extruder 104 at barrel C9 after the foaming agent is first mixed with a polyol/surfactant mixture.

[0036] Catalyst is preferably introduced into the extruder 104 via an extruder head 120 from reservoir 156. A cross-sectional side view of the extruder head 120 of the extrusion system is shown in Figure 2.

[0037] In making foam, the mixture of the component parts of the graphite particles, isocyanate, polyol, and additional materials, without the catalyst, arrives via a hose 200 (shown in Figure 1) to an entry port 202 in a mixing block 204 of the extruder head 120. At mixing block 204, the component mixture travels via a worm gear 206 to agitator 208 located in a cavity area 210. Concurrently, catalyst enters at a catalyst port 214 and travels along a duct 215 to arrive in the cavity area 210 via a catalyst entry port 216. The mixture of the component parts of the expandable graphite isocyanate, polyol and additional agents and catalyst are mixed together by agitator 208 in the cavity area 210 and continues out of the cavity area 210, preferably onto a conveyor system such as the conveyor illustrated in U.S. Patent No. 5,723,506. Preferably, the cavity 210 is 2 to 3 inches wide and the agitator is rotated at approximately 3500 to 5500 rpm.

[0038] A preferred method of manufacturing foam using the extruder of Figure 1 includes feeding graphite particles and/or carbon-black from source 150 to the extruder 104 at barrel C1. A mixture of isocyanate, dispersing agent and surfactant is fed to the extruder 104 at barrel C2 from reservoir 151. Additional graphite particles and/or carbon-black may be added from source 152 and fed to the extruder 104 at barrel C4 particularly, when loading of the graphite particles and/or carbon-black is to exceed 12-15%. An additional mixture of isocyanate, dispersing agent and surfactant is then added to the

extruder 104 at barrel C6 from reservoir 153. Blowing agent is provided to the extruder 104 at barrel C8 from reservoir 154. Polyol, foaming and blowing agent, surfactant and curing agent are fed to the extruder 104 at barrel C9 from reservoir 155. Finally, a catalyst or catalyst mixture is provided to the extruder head 120 from reservoir 156.

[0039] A preferred method of manufacturing an isocyanate dispersion in accordance with the teachings of the present invention using the extruder of Figure 1 includes feeding graphite particles and/or carbon black from source 150 to the extruder 104 at barrel C1. A mixture of isocyanurate and dispersing agent, optionally with surfactant, is fed to the extruder 104 at barrel C2 from reservoir 151. Additional graphite particles and/or carbon black may be added from reservoirs 152 and fed to the extruder 104 at barrel C4. An additional mixture of isocyanurate and dispersing agent, optionally with surfactant, may then be added to the extruder 104 at barrel C6 from reservoir 153. No polyol or catalyst materials are added to the extruder and the resultant dispersion exits the extruder at the last barrel C12 and is preferably directed into an appropriate container, bypassing the extruder head 202.

[0040] A preferred method of manufacturing a polyol dispersion in accordance with the present invention using the extruder of Figure 1 includes feeding graphite particles and/or carbon black from source 150 and/or source 152 to the extruder 104 at barrel C1 and/or barrel C4. A mixture of polyol and a dispersing agent optionally with foaming agent, blowing agent, surfactant and/or curing agent, is fed to the extruder 104 at barrel C9 from reservoir 155. The polyol dispersion exits the extruder at barrel C12, preferably directly into an appropriate container, bypassing the extruder head 202.

[0041] The production of foams based on isocyanates is known per se and is described, for example, in German Offenlegungsschriften 1,694,142, 1,694,215 and 1,720,768, as well as in *Kunststoff-Handbuch* [Plastics Handbook], Volume VII, Polyurethane, edited by Vieweg and Hochtlen, Carl Hanser Verlag, Munich 1966, and in



the new edition of this tome, edited by G. Oertel, Carl Hanser Verlag, Munich, Vienna, 1983.

[0042] These foams are mainly those that comprise urethane and/or isocyanurate and/or allophanate and/or uretdione and/or urea and/or carbodiimide groups. Preferred starting components include aliphatic, cycloaliphatic, araliphatic, aromatic and heterocyclic polyisocyanates, such as those described, for example, by W. Siefken in Justus Liebigs Annalen der Chemie, 562, pp. 75-136, for example, those of the formula



in which n denotes 2-4, preferably 2-3, and Q denotes an aliphatic hydrocarbon radical of 2-18, preferably 6-10 carbon atoms, a cycloaliphatic hydrocarbon radical of 4-15, preferably 5-10 carbon atoms, an aromatic hydrocarbon radical of 6-15, preferably 6-13 carbon atoms or an araliphatic hydrocarbon radical of 8-15, preferably 8-13 carbon atoms, for example, such polyisocyanates as described in DE-OS 2,832,253, pp. 10-11.

[0043] Particularly preferred are usually those polyisocyanates which are technically readily accessible, for example, the 2,4- and 2,6-toluylene diisocyanate as well as any mixture of these isomers ("TDI"); polyphenyl polymethylenepolyisocyanates, such as those obtained by an aniline formaldehyde condensation and subsequent treatment with phosgene ("crude MDI"), and polyisocyanates comprising carbodiimide groups, urethane groups, allophanate groups, isocyanurate groups, urea groups or biuret groups ("modified polyisocyanates"), especially those modified polyisocyanates which are derived from 2,4- and/or 2,6-toluylene diisocyanate and from 4,4'- and/or 2,4'-diphenylmethane diisocyanate.

[0044] The starting components may further be compounds of a molecular weight usually of 400 to 10,000, containing at least two hydrogen atoms reactive toward isocyanates. These comprise, besides compounds containing amino, thio, or carboxyl groups, preferably compounds containing hydroxyl groups, in particular compounds containing 2 to 8 hydroxyl groups, especially those of a molecular weight of 1,000 to

6,000, preferably 2,000 to 6,000, for example polyethers and polyesters as well as polycarbonates and polyester amides containing at least 2, usually 2 to 8, preferably 2 to 6 hydroxyl groups; these compounds are known per se for the preparation of homogenous and cellular polyurethanes and are disclosed, for example in DE-OS 2,832,253, pp. 11-18.

[0045] When appropriate, compounds comprising at least two hydrogen atoms reactive toward isocyanates and of a molecular weight of 32 to 399 may be used as further starting components. Also, in this case, compounds containing hydroxyl groups and/or amino groups and/or thiol groups and/or carboxyl groups, preferably compounds containing hydroxyl groups and/or amino groups, are understood to be those which are used as chain lengtheners or crosslinking agents. These compounds usually have 2 to 8, preferably 2 to 4 hydrogen atoms reactive toward isocyanates. Appropriate examples are disclosed in DE-OS 2,832,253, pp. 19-20. Other examples of polyisocyanates and polyols useful in the invention are described in U.S. Patent No. 5,149,722, co-owned by the assignee of the present invention and incorporated herein by reference as if fully set forth.

[0046] Blowing agents which may be used to make foam include water and/or readily volatile inorganic or organic substances and other auxiliary volatile blowing agents typically used to blow PUR/PIR foams. Water, however, used in small quantities serves as a foaming agent where other blowing agents are used.

[0047] Organic blowing agents include acetone, ethylacetate; halogen-substituted alkanes, such as methylene chloride, chloroform, ethylidene chloride, vinylidene chloride, monofluoro trichloromethane, chlorodifluoromethane, dichlorodifluoromethane, dichlorodifluoroethane, dichlorotrifluoroethane; also halogenated and non-halogenated hydrocarbon blowing agents.

[0048] Specific examples of non-halogenated hydrocarbon blowing agents include: pentane, butane, hexane, heptane, diethyl ether, isopentane, n-pentane and cyclopentane.

[0049] Specific examples of halogenated hydrocarbon blowing agents include: 1,1,1,4,4,4-hexafluorobutane (HFC-356); 1,1-dichloro-1 fluoroethane (HFC-141b); the tetrafluoroethanes such as 1,1,1,2-tetrafluoroethane (HFC-134a); the pentafluoropropanes such as 1,1,2,2,3 pentafluoropropane (HFC-245ca), 1,1,2,3,3-pentafluoropropane (HFC 245ea), 1,1,1,2,3-pentafluoropropane (HFC-245eb), and 1,1,1,3,3 pentafluoropropane (HFC-245fa); the hexafluoropropanes such as 1,1,2,2,3,3-hexafluoropropane (HFC-236ca), 1,1,1,2,2,3-hexafluoro propane (HFC-236cb), 1,1,1,2,3,3-hexafluoro-propane (HFC-236ea), 1,1,1,3,3,3-hexafluoropropane (HFC-236fa); the pentafluorobutanes such as 1,1,1,3,3-pentafluorobutane (HFC-365); and difluoroethanes such as 1,1-difluoroethane (HFC-152a).

[0050] Inorganic blowing agents are, for example, air, CO<sub>2</sub> or N<sub>2</sub>O. A blowing effect may also be obtained by adding compounds which decompose at temperatures above room temperature giving off gases, such as azodicarbonamide or azoisobutyronitrile. Other examples of blowing agents may be found in *Kunststoff-Handbuch*, Vol. VII, by Vieweg and Hochtlen, Carl-Hanser Verlag, Munich, 1966, on pages 108 and 109, 453 to 455 and 507 to 510.

[0051] Different types of blowing agents are used in combination, but use of a non-halogenated hydrocarbon chemical as the primary blowing agent has generally been avoided due to the flammability of foams which conventionally result. Use of expandable graphite as taught by the present invention permits the use of a non-halogenated primary blowing agent in the production of foam which is rated as Factory Mutual Class 1 when tested using test method ASTM E84.

[0052] When appropriate, other auxiliary agents and additives may be used at the same time, such as:

- water and/or other highly volatile organic substances as propellants, i.e. foaming agents;

- additional catalysts of the type known per se in amounts up to 10% by weight of the polyol component;

- surface-active additives, such as emulsifiers and foam stabilizers, and

- reaction retardants, for example acidic substances such as hydrochloric acid or organic acid halides, also cell regulators of the type known per se, such as paraffins or fatty alcohols or dimethylpolysiloxanes, as well as, pigments or dyes and other flame retardants of the type known per se, for example tricresyl phosphate, also stabilizers against the effect of aging and weathering, plasticizers and fungistats and bacteriostats as well as fillers such as barium sulphate, kieselguhr, carbon black, expanded or expandable microspheres or whiting.

[0053] Other examples of surface active additives, foam stabilizers, cell regulators, reaction retardants, stabilizers, flame retardants, plasticizers, dyes, fillers, fungistats, bacteriostats to be used at the same time if appropriate, as well as details concerning the use and action of these additives are described in *Kunststoff-Handbuch* [Plastics Handbook], Volume VII, edited by Vieweg and Hochtlen, Carl Hanser Verlag, Munich 1966, for example on pages 103-113.

[0054] Figures 3-5 reflect various foams, Examples 1-4, made in accordance with the extrusion method recited above. A non-halogenated hydrocarbon blowing agent, pentane, was the blowing agent used in all Examples 1-4.

[0055] Example 1 reflects a control example with no expandable graphite material. By comparison, the other examples were made with differing amounts of expandable graphite having an average particle size of less than 200 microns. Burn tests were performed with the control foam, Example 1, and expandable graphite foams, Examples 2-4. Thickness and weight loss examples were measured.

[0056] Visually, polyisocyanurate foam made with the non-halogenated blowing agent and a 5% loading or higher of expandable graphite, Examples 2-4, produced no noticeable black smoke as with polyisocyanurate made with the non-halogenated blowing

agent and a standard liquid flame retardant, Example 1. There was no significant density increase using expandable graphite in the range of 5%-12%. There was also considerably less flame spread noticed during the burn with 5% or more of graphite particles.

[0057] Based on the test results, it was determined that fire retardant foams can be produced by providing 1% to 50% by weight evenly dispersed expandable graphite particles which have an average particle size of less than 200 microns. Moreover, the use of such expandable graphite in a preferred range of 3% - 20% by weight can produce a class 1 rated foam per Factory Mutual Standard F.M. 4450 and Underwriters Laboratories Standard UL1256 when tested using test method ASTM E84.

[0058] Tables 6-7 reflect an additional comparative analysis, Examples 5-7, of a control versus two example foams made in accordance with the teachings of the present invention. Control Example 5 contained no expandable graphite. Example 6 contained expandable graphite and Example 7 contained a combination of expandable graphite and carbon black. In all cases, the primary blowing agent was a non-halogenated hydrocarbon chemical. Less than 1% of a halogenated hydrocarbon co-blowing agent and less than 1% water serving as a foaming agent were used in Examples 6 and 7.

[0059] As reflected in Table 7, the foam made in accordance with Example 7 had the best K factor and was otherwise comparable to prior art commercial foam, Foam II, made with a halogenated hydrocarbon blowing agent. The foam made in accordance with Example 6 had a K factor better than the prior art competitive foam, Foam I, made with a non-halogenated primary blowing agent, but not quite as good as the prior art foam, Foam II, made with a non-halogenated primary blowing agent. However, unlike the prior art foam made with a non-halogenated primary blowing agent, Foam I, the Example 6 foam passed Factory Mutual Standard F.M. 4450 and Underwriter's Laboratory Standard UL1256 for a Class 1 rating when tested in accordance with Test Method ASTM E84.

[0060] Based on the results of Examples 2, 3, 4 and 6, it is believed that the Example 7 foam will also be accorded a Factory Mutual Class 1 rating when independently tested in accordance with Test Method ASTM E84.

[0061] In accordance with the experimentation and testing performed by the present inventors, preferred formulations for the manufacturer of PUR/PIR boardstock and bunstock are set forth in Figures 8 and 9, respectively. While preferred types and/or sources of the component materials are identified, these are non-limiting examples. Various other additive materials as discussed above, preferably not exceeding 100 parts by weight, may be added to the formulations set forth in Figures 8 and 9. These PIR/PUR foam formulations are primarily characterized in the use of at least 3% expandable graphite preferably having an average particle size less than 200 microns, the use of a non-halogenated hydrocarbon chemical or blend as the primary blowing agent, and the use of less than 1% of a halogenated blowing agent. The use of at least 4.5% expandable graphite and 3.5% carbon black can produce a class 1 rated foam per Factory Mutual Standard F.M. 4450 and Underwriters Laboratories Standard UL1256 when tested using test method ASTM E84.

[0062] Preferably, the components are combined by the use of an extruder as set forth above. Alternatively, the components can be mixed utilizing other methods. Where conventional mixing is employed, it is preferred to create either a polyol or isocyanate dispersion with the expandable graphite and optionally carbon black which is then used to make foam in accordance with the formulations set forth in Figures 8 and 9.

[0063] Figure 10 sets forth preferred dispersion formulations in this regard. Dispersions so made can be stored and/or shipped to other locations with minimal effect on the uniformity of the distribution of the expandable graphite particles in the dispersion. This permits a single extruder to supply many batch processing facilities to make foam in accordance with one of the preferred methods taught by the present invention.

\* \* \*

## CLAIMS

What is claimed is:

1. A rigid polyurethane and/or polyisocyanurate foam having fire resistance comprising:

from 1 - 50 % by weight of evenly dispersed expandable graphite particles having an average particle size less than 200 microns and from 99 to 50 % by weight of a closed cell polyurethane foam.

2. A rigid polyurethane or polyisocyanurate foam according to claim 1 wherein the expandable graphite particles comprise 3 to 20 % by weight of the foam and have a PH greater than 5.

3. The foam of claim 2 which passes the burning test of Factory Mutual Standard F.M. 4450 and Underwriters Laboratories standard UL 1256 for class 1 ratings when tested in accordance with test method ASTM E84.

4. A rigid polyurethane or polyisocyanurate foam according to claim 1 having at least 4.5 % by weight expandable graphite particles and at least 3.5 % by weight carbon black.

5. The foam of claim 4 which passes the burning test of Factory Mutual Standard F.M. 4450 and Underwriters Laboratories standard UL 1256 for class 1 ratings when tested in accordance with test method ASTM E84.

6. The foam according to claim 2 wherein the expandable graphite particles are GRAFguard 160-80-N expandable graphite.

7. A polyurethane and/or polyisocyanurate foam having fire resistance made using at least 3 % by weight expandable graphite and a non-halogenated hydrocarbon chemical or a non-halogenated hydrocarbon chemical blend as a primary blowing agent.

8. The foam according to claim 7 wherein the expandable graphite particles are GRAFguard 160-80-N expandable graphite.

9. The foam according to claim 7 wherein the primary blowing agent is selected from the group consisting of pentane, butane, hexane, heptane, diethyl ether, isopentane, n-pentane and cyclopentane or blends of chemicals from said group.

10. A rigid polyurethane and/or polyisocyanurate foam made according to claim 7 by mixing:

10.57 to 41.14 PBW expandable graphite particles having an average particle size less than 200 microns;

191 to 400 PBW isocyanate;

75 to 125 PBW polyol;

16 to 36 PBW of a non-halogenated hydrocarbon chemical or a non-halogenated hydrocarbon chemical blend as a primary blowing agent;

0 to 20.57 PBW of carbon black; and

19 to 165 PBW other ingredients with less than 1% by weight of halogenated blowing agents.

11. The foam of claim 10 which passes the burning test of Factory Mutual Standard F.M. 4450 and Underwriters Laboratories standard UL 1256 for class 1 ratings when tested in accordance with test method ASTM E84.



12. A rigid polyurethane and/or polyisocyanurate foam made according to claim 7 by mixing:

14 to 40 PBW expandable graphite particles having an average particle size less than 200 microns;

192 to 500 PBW isocyanate;

75 to 125 PBW polyol;

5 to 46 PBW of a non-halogenated hydrocarbon chemical or a non-halogenated hydrocarbon chemical blend as a primary blowing agent;

0 to 20 PBW of carbon black; and

20 to 155 PBW other ingredients with less than 1% by weight of halogenated blowing agents.

13. The foam of claim 12 which passes the burning test of Factory Mutual Standard F.M. 4450 and Underwriters Laboratories standard UL 1256 for class 1 ratings when tested in accordance with test method ASTM E84.

14. A method for facilitating the manufacture of fire resistant polyurethane and/or polyisocyanurate foam comprising:

introducing 10.57 to 41.14 PBW expandable graphite particles having an average particle size less than 200 microns to the screw of an extruder;

introducing at least 2 PBW of a dispersing agent to the screw of the extruder; and

using the screw of the extruder to mix the expandable graphite particles and dispersant with either 191 to 500 PBW of a isocyanate or 75 to 125 PBW of a polyol.

15. The method of claim 14 wherein 95 to 105 PBW of polyol are introduced to the screw of the extruder; 14 to 32 PBW of the expandable graphite particles are introduced to the screw of the extruder; 0 to 16 PBW of carbon black is introduced to the screw of the extruder; 3 to 4 PBW of the dispersing agent is introduced to the screw of

the extruder; and 0 to 50 PBW of other non-reactive ingredients are introduced to the screw of the extruder to produce a polyol dispersion.

16. The method according to claim 14 wherein 231 to 251 PBW of isocyanate is introduced to the screw of the extruder; 14 to 32 PBW of the expandable graphite particles are introduced to the screw of the extruder; 0 to 16 PBW of carbon black is introduced to the screw of the extruder; and 3 to 4 PBW of the dispersing agent is introduced to the screw of the extruder; and 0 to 100 PBW of other non-reactive ingredients are introduced to the screw of the extruder to produce an isocyanate dispersion.

17. The method according to claim 14 wherein:

10.57 to 41.14 PBW of expandable graphite particles having an average particle size less than 200 microns are introduced to the screw of the extruder;

191 to 400 PBW of isocyanate is introduced to the screw of the extruder;

75 to 125 PBW of polyol is introduced to the screw of the extruder;

16 to 36 PBW of a non-halogenated hydrocarbon chemical or a non-halogenated hydrocarbon chemical blend as a primary blowing agent is introduced to the screw of the extruder;

0 to 20.57 PBW of carbon black are introduced to the screw of the extruder; and

19 to 165 PBW other ingredients with less than 1 PBW of halogenated blowing agents are introduced to the screw or an extrusion head of the extruder to produce rigid foam boardstock.

18. The method according to claim 14 wherein:

14 to 40 PBW of expandable graphite particles having an average particle size less than 200 microns are introduced to the screw of the extruder;

192 to 500 PBW isocyanate is introduced to the screw of the extruder;

75 to 125 PBW polyol is introduced to the screw of the extruder;

5 to 46 PBW of a non-halogenated hydrocarbon chemical or a non-halogenated hydrocarbon chemical blend as a primary blowing agent is introduced to the screw of the extruder;

0 to 20 PBW of carbon black is introduced to the screw of the extruder; and

20 to 155 PBW other ingredients with less than 1% by weight of a halogenated blowing agent are introduced to the screw or an extrusion head of the extruder to produce rigid foam bunstock.

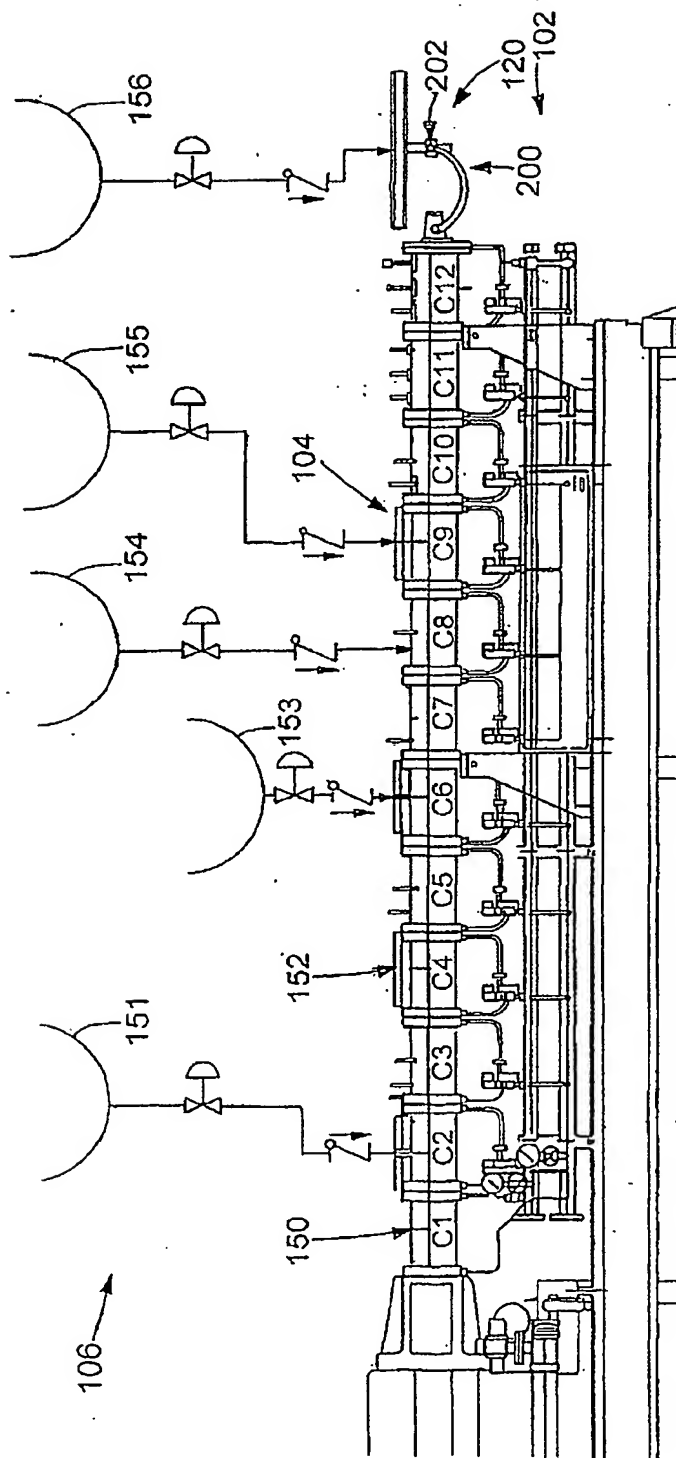
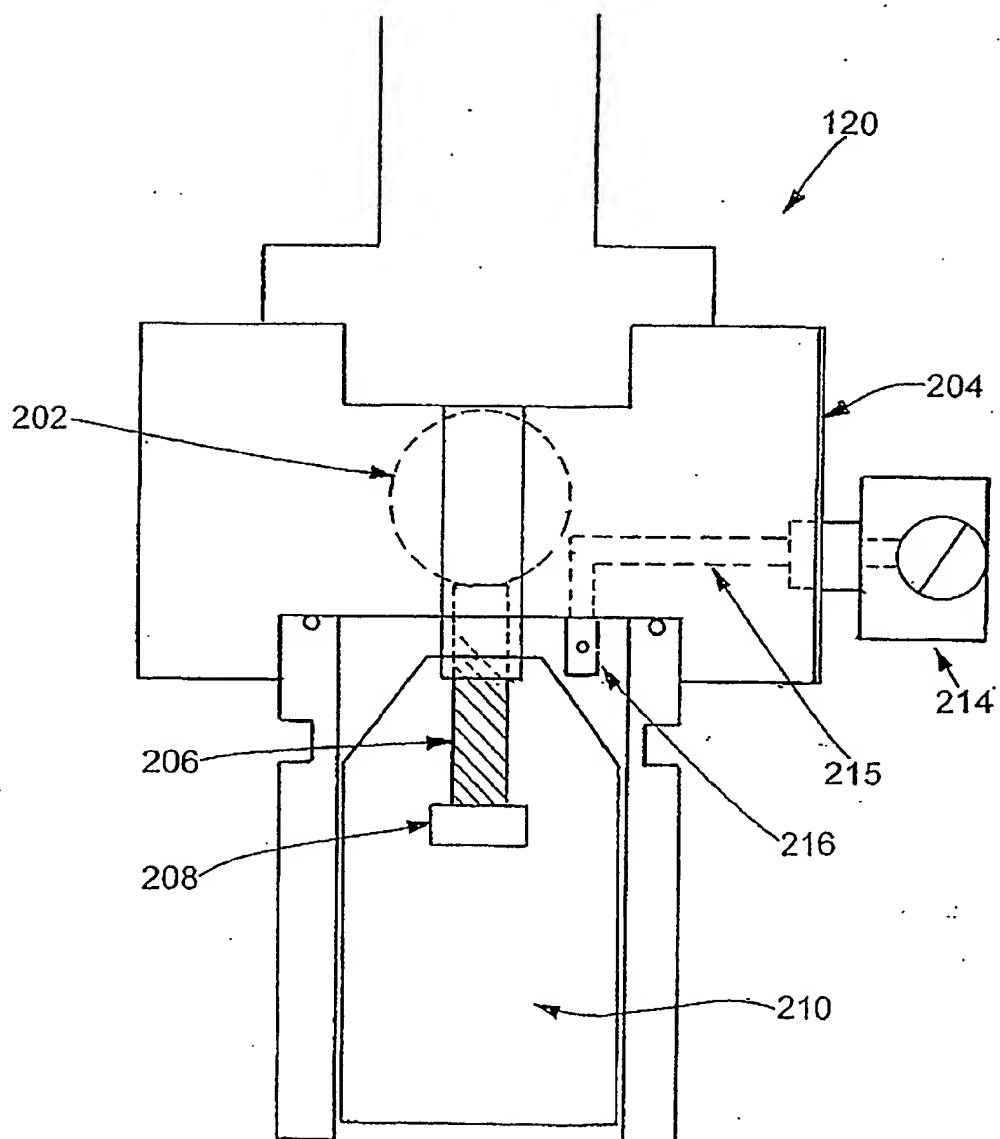


Fig. 1

Fig. 2



CHEMICAL (Extruder Location)	PRODUCT	Example 1		
		PBW	%	LBS.
Isocyanate (C2/C6)	Bayer	211.05	58.584	50.89
Polyol (C9)	Stepan	100	27.759	24.11
Expandable Graphite	N/A	0	0.000	0.00
Fire Retardant (C9)	Antiblaze 80	10	2.776	2.41
Blowing Agent (C8)	Pentane	10.0	2.776	2.41
Blowing Agent (C9)	Pentane	20.0	5.552	4.82
Surfactant (C2/C6)	Goldsmith	1.0	0.278	0.24
Surfactant (C7)	Goldsmith	2	0.555	0.48
Water (C9)		1	0.278	0.24
K Octoate (120)	HEX-CEM	4.00	1.110	0.96
Amine (120)	Polycat 18	0.08	0.022	0.02
Acetate (120)	Polycat 46	1.12	0.311	0.27
Totals		360.2	100	86.9

Fig. 3

CHEMICAL (Extruder Location)	PRODUCT	Example 2			Example 3			Example 4		
		PBW	%	LBS.	PBW	%	LBS.	PBW	%	LBS.
Isocyanate (C2/C6)	Bayer	204.61	56.552	49.12	204.61	54.737	47.55	204.61	52.356	45.48
Polyol (C9)	Stepan	100	27.639	24.01	100	26.751	23.24	100	25.588	22.23
Exp. Graphite (C1/C4)	GG 160-80-N	18	4.975	4.32	30	8.025	6.97	47	12.026	10.45
Fire Retardant	N/A	0	0.000	0.00	0	0.000	0.00	0	0.000	0.00
Blowing Agent (C8)	Pentane	10.0	2.764	2.40	10.0	2.675	2.32	10.0	2.559	2.22
Blowing Agent (C9)	Pentane	20.0	5.528	4.80	20.0	5.350	4.65	20.0	5.118	4.45
Surfactant (C2/C6)	Goldsmith	1.0	0.276	0.24	1.0	0.268	0.23	1.0	0.265	0.22
Surfactant (C7)	Goldsmith	2	0.535	0.48	2	0.535	0.46	2	0.512	0.44
Water (C9)		1	0.276	0.24	1	0.268	0.25	1	0.256	0.22
K Octoate (120)	HEX-CHEM	4.00	1.106	0.96	4.00	1.070	0.93	4.00	1.024	0.89
Amine (120)	Polycat 18	0.08	0.022	0.02	0.08	0.021	0.02	0.08	0.020	0.02
Acetate (120)	Polycat 46	1.12	0.310	0.27	1.12	0.300	0.26	1.12	0.287	0.25
Totals		361.81	100	86.86	373.8	100	86.88	390.8	100	86.87

Fig. 4

FOAM CHARACTERISTICS				
	Example 1	Example 2	Example 3	Example 4
Density (lbs./cu. ft.)	1.89	1.90	1.93	1.95
Burn Test Results				
Type of Smoke	Thick Black	Light Opaque	Light Opaque	Light Opaque
Self-Extinguishing	No	Yes	Yes	Yes
Protective Char Formed	No	Yes	Yes	Yes

Fig. 5

PREFERRED DISPERSION FORMULATIONS				
Component	Polyol Dispersion		ISO Dispersion	
	PBW	Range	PBW	Range
Isocyanate (MRP, Bayer)	0		241	$\pm 10$
Polyester Polyol (Stepan 2352)	100.00	$\pm 5$	0	
Exp. Graphite (160-80-N, Graph-Tech Inc)	15.00	$\pm 1.0$	15.00	$\pm 1.0$
Exp. Graphite (160-80-N, Graph-Tech Inc) or Carbon Black	15.00	$\pm 1.0$	15.00	$\pm 1.0$
Dispersing Agent (Pelron 344, ethoxylated phenol)	3.50	$\pm 0.5$	3.50	$\pm 0.5$
Other Non-reactive Ingredients	0	+50	0	+100

Fig. 10



<b>Extruder Made Isocyanurate Foam</b>			
<b>Formulation Examples</b>	<b>Ex. 5</b>	<b>Ex. 6</b>	<b>Ex. 7</b>
<b>Component</b>	<b>PBW</b>	<b>PBW</b>	<b>PBW</b>
Isocyanate (MRP, Bayer)	219.00	241.00	231.00
Polyester Polyol (Stepan 2352)	100.00	100.00	100.00
Expandable Graphite (GG160-80-N, Graph-Tech Inc)	0.00	31.20	20.00
Carbon Black (Cabot Ind.)	0.00	0.00	15.00
Phosphate (Antiblaze 80, Albright & Wilson)	10.00	15.00	7.50
Brominate-Ester (Pelron, Ele Corp.)	10.00	7.50	7.50
50/50 Blend Iso-Pentane/Cyclopentane (Exxon)	26.00	26.00	28.00
134-a,HFC (Dupont)	0.00	3.50	2.00
Surfactant (Goldsmidt 8457,8469)	1.40	2.00	2.50
Dispersing Agent ( Pelron 344, Ele Corp.)	0.00	2.90	2.50
WATER	0.00	0.75	0.50
Pottasium Octoate (HexCem 977 Mooney Chemicals)	5.00	6.00	6.00
P-5,Amine (Polycat 5, Air Products)	0.15	0.12	0.12
Pottasium Acetate (Pelron Inc)	1.45	1.60	1.60

**Fig. 6**

FOAM CHARACTERISTICS					
	Example 5	Example 6	Example 7	Prior Art* Foam I	Prior Art** Foam II
K-Factor (initial)	0.163	0.163	0.154		
(10 day)		0.178	0.156		
(30 day)	0.18	0.178	0.157	0.18	0.17
Closed Cell %	92.4	90.5	88.9	89.5	94
Friability % Wt. Loss	2.5	8.9	37.8		6.5
Core Density (lbs/cu. ft.)	1.89	1.85	1.92	1.75	1.73
Cold Box % Change (7 day)	0.34	No Change	0.33		0.33
Humid. Aging % Change MD (7 day)	0.85	0.22	No Change		0.55
Humid. Aging % Change XMD (7 day)	0.9	0.25	No Change		0.45
Compressive Strength (psi)	20.6	24.6	21.6	24.2	20.1
Factory Mutual Class 1	No	Yes	Pending	No	Yes

\* Made with Iso-Pentane/Cyclopentane Blend as Primary Blowing Agent

\*\* Made with (HCFC-141b) as Primary Blowing Agent

**Fig. 7**

PREFERRED BOARDSTOCK FORMULATIONS				
Component	PBW	Min	Max	Pounds
Isocyanate (MRP, Bayer)	241.33	191	400	551.16
Polyester Polyol (Stepan 2352)	100.00	75	125	228.38
Expandable Graphite Particles < 200 $\mu$ ave. size (Graph-Tech Inc)	15.57	10.57	20.57	35.56
Expandable Graphite Particles < 200 $\mu$ ave. size (Graph-Tech Inc) or Carbon Black	15.57	10.57	20.57	35.56
Phospate/Phosphate Blends (Antiblaze 80, Albright & Wilson)	15.00	10	35	34.26
Brominated-Ester (Pelron)	<u>7.50</u>	<u>0</u>	<u>10</u>	<u>17.13</u>
Additional Fire Retardants	22.5	10	45	51.39
Halogenated Hydrocarbon (134-a,HFC, DuPont)	3.50		4.5	7.99
Non-Halogenated Hydrocarbon (Pentane, Iso-Cyclopentane Blends, Exxon)	26.00	16	36	59.38
Surfactant (8469 Goldsmith)	2.00	1	4	4.57
Dispersing Agent (Pelron 344)	2.90	0	4.4	6.62
Foaming Agent (WATER)	0.75	0	1.5	1.71
Pottasium Octoate	6.00	3	9	13.70
P-5,Amine (Polycat 5, Air Products)	0.12	0.07	0.17	13.70
Pottasium Acetate	<u>1.62</u>	<u>0.87</u>	<u>2.37</u>	<u>3.70</u>
Catalysts	7.74	3.94	11.54	31.1
Other Ingredients	0	0	100	
	Total LBS			1000.00

Fig. 8

<b>PREFERRED BUNSTOCK FORMULATIONS</b>				
<b>Component</b>	<b>PBW</b>	<b>Min</b>	<b>Max</b>	<b>Pounds</b>
Isocyanate (MRP, Bayer)	242.17	192	500	554.26
Polyester Polyol (Kosa 2031 or Stepan 3152)	100.00	75	125	228.87
Expandable Graphite Particles < 200 $\mu$ ave. size (Graph-Tech Inc)	15.57	14	20	35.64
Expandable Graphite Particles < 200 $\mu$ ave. size (Graph-Tech Inc) or Carbon Black	15.57	14	20	35.64
Phosphate / Polymeric Phosphate, amine blends (Antiblaze 80, Albright&Wilson)	15.00	10	25	34.33
Brominated-Ester (Pelron)	<u>7.50</u>	<u>0</u>	<u>10</u>	<u>17.17</u>
<b>Additional Fire Retardants</b>	<b>22.5</b>	<b>10</b>	<b>35</b>	<b>51.5</b>
Halogenated Hydrocarbon (134-a,HFC, DuPont)	3.50		4.5	8.01
Non-Halogenated Hydrocarbon (Iso-Pentane, Exxon)	26.00	5.0	46	59.51
Surfactant (84PI, Goldsmith)	2.50	1.5	4.5	5.72
Dispersing Agent (Pelron 344)	2.90	0	4.4	6.64
Crosslinker (Epoxy Resin, Epon 828)	3.79	2.0	4.5	8.67
Trymer Catalyst (TMR-3, Air Products) Quarternary ammonium salt	1.33	1.0	2.5	3.04
DMEA, Amine	0.55	.25	1.0	1.25
DEG, Glycol	<u>0.55</u>	<u>.25</u>	<u>1.0</u>	<u>1.25</u>
<b>Catalysts</b>	<b>2.43</b>	<b>1.5</b>	<b>4.5</b>	<b>5.54</b>
Other Ingredients	0	0	100	0
	<b>Total LBS</b>			<b>1000.00</b>

Fig. 9

# INTERNATIONAL SEARCH REPORT

Int. application No.  
PCT/US01/09626

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(7) : CO8G 18/00; CO8J 9/00, 9/14 US CL : 521/ 99, 131,155, 170 According to International Patent Classification (IPC) or to both national classification and IPC				
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 521/ 99, 131,155, 170 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)				
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
Y	US 4,795,763 A (GLUCK et al.) 03 January 1989, see the entire document	1-18		
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.				
<table border="0"> <tr> <td>           * Special categories of cited documents:            "A" document defining the general state of the art which is not considered to be of particular relevance            "B" earlier document published on or after the international filing date            "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)            "O" document referring to an oral disclosure, use, exhibition or other means            "P" document published prior to the international filing date but later than the priority date claimed         </td> <td>           "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention            "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone            "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art            "Z" document member of the same patent family         </td> </tr> </table>			* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "B" earlier document published on or after the international filing date "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "B" earlier document published on or after the international filing date "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family			
Date of the actual completion of the international search 27 JUNE 2001		Date of mailing of the international search report 13 JUL 2001		
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3330		Authorized officer JOHN COONEY <i>John Cooney</i> Telephone No. (703) 308-0651		